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Studies on the Devitrification of the Glasses of the System LiO-ZnO-AlO-SiO

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ABSTRACTS

deformation or surface crazing of the sample during reheating. The limit of the amount of addition in mol% for each of the oxides varied with the own property of the oxides as follows:

(1) For each of the series of alkali- and alkaliearth-oxide, which acts as the glass network modifier in the glass structure, the limit decreases with the increase of the size of cation, *i. e.*,

The value of limit: $\text{NaO}_{0.5} > \text{KO}_{0.5} > \text{RbO}_{0.5}$, $\text{MgO} > \text{CaO} > \text{SrO} > \text{BaO}$.

For the oxides with the cation of about the same size but of the different valency, the oxide with the cation of the higher valency has always the higher limit, *i. e.*,

The value of limit: $\text{CaO} > \text{NaO}_{0.5}$, $\text{SrO} > \text{KO}_{0.5}$, $\text{BaO} > \text{RbO}_{0.5}$.

(2) For the glass network formers ($\text{BO}_{1.5}$, $\text{AlO}_{1.5}$, $\text{PO}_{2.5}$, and $\text{AsO}_{2.5}$) and also for the intermediates (BeO , PbO , CdO , ZrO_2 , CeO_2 , $\text{LaO}_{1.5}$) the limit was generally low compared with that for the glass network modifiers, with the exception for the oxides of transition element (TiO_2 , $\text{MnO}_{1.5}$, $\text{VO}_{2.5}$, $\text{CrO}_{1.5}$, $\text{FeO}_{1.5}$, CoO , NiO).

The structural explanations were made of the above results in terms of the polarizing power, and the ability of strengthening the glass network, of the cation in the oxides introduced.

Studies on the Devitrification of the Glasses of the System $\text{Li}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$

Sumio SAKKA and Megumi TASHIRO

Yogyo Kyokaishi (Journal of the Ceramic Association, Japan), **69**, 109 (1961)

Studies were carried out for the purpose of finding out the range of compositions in the system $\text{Li}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$, in which the change by reheating to polycrystalline bodies occurs without accompanying the defects as flaw and crease, and of measuring properties of the devitrified glasses.

The results obtained are as follows:

1) Changing the Li_2O content as 4, 6, 8, 12 and 16 against $\text{ZnO} + \text{Al}_2\text{O}_3 + \text{SiO}_2 = 100$ the range, in which the batches may be melted at $1300\sim 1400^\circ\text{C}$ to clear glasses and produce perfect polycrystalline specimens by reheating, was determined.

2) Occasionally, above specimens supported by two knife edges deformed by their own weight during the reheating. When Li_2O content was as low 4, 6, 8 the amount of ZnO has proved to be most influential in the deformation, and it was confirmed that such trend was becoming smaller with the increasing amount of ZnO .

3) The differential thermal and X-ray analyses have disclosed that from the specimens of low Li_2O (4, 6, 8) the primary crystals were ZnO -compounds such as $2\text{ZnO}\cdot\text{SiO}_2$, while from those of high Li_2O the primary crystalline phase was composed of lithium compounds such as $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$.

When the reheating was carried out at higher temperatures, *i. e.*, $50\sim 100^\circ\text{C}$

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below the deformation temperature of polycrystalline specimens, the crystals were composed of willemite, β -eucryptite, β -spodumene, cristobalite, quartz, and lithium mono- and di-silicates, having the size of $1\sim 2\mu$ measured under microscope.

4) The bending strength of polycrystalline specimens changed in a high degree by composition. Although there seemed to exist no simple relation between the composition and the bending strength, the values of those of low alkali ($\text{Li}_2\text{O} = 4, 6, 8$) and $\text{Al}_2\text{O}_3 = 0$ gave the exceptionally low values, which probably due to the existence of minute hair cracks came from the abnormal volume change at around 250°C of cristobalite formed in large amount in the specimens during the reheating.

5) The amount of Al_2O_3 produced a large effect on the thermal expansion of the specimens in the composition range given above. There was a trend that the expansion coefficient became smaller with the increase of Al_2O_3 content. Especially, high Al_2O_3 glasses containing small amount of Li_2O ($=4$ and 6) gave the products having exceedingly low expansion coefficient (5.4×10^{-7}). The specimens of $\text{Al}_2\text{O}_3 = 0$ have larger expansion coefficient. This may be interpreted by the formation of cristobalite having large expansion coefficient instead of β -eucryptite which lowers the expansion of devitrified products.

The Effects of Heat Treatment on the Strength of Polycrystalline Material Produced from the Glass of the System $\text{Li}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$

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Yogyo Kyokaishi (Journal of the Ceramic Association, Japan), 69, 35 (1961)

In the previous paper (*J. Ceram. Assoc. Japan*, 68 [10] 223 (1960)) the authors reported that some glasses of low lithium content (4%) in the system $\text{Li}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ could be converted, by the heat treatment, into a polycrystalline material without showing any appreciable deformation even if no special nucleating agent, such as platinum, was added. The present paper contains the results of experiments designed to determine the optimum conditions of heat treatment of the glass of this type for producing a polycrystalline material of high mechanical strength.

(1) **Chemical composition of the glass studied.** The glasses of the composition, $\text{MgO } x, \text{Al}_2\text{O}_3 \ y, \text{SiO}_2 \ z, \text{Li}_2\text{O } 4$, where $x+y+z=100$ by weight, were melted and formed into a specimen of the size $2.5 \times 5 \times 50$ mm. They were heated from room temperature to 1200°C with the rate of $5^\circ\text{C}/\text{min.}$ and then held there for two hours. Among the polycrystalline materials, the one produced from a glass of the composition of $\text{Li}_2\text{O } 4, \text{MgO } 15, \text{Al}_2\text{O}_3 \ 23, \text{SiO}_2 \ 62$ showed the highest modulus of rupture ($1,550 \text{ kg}/\text{cm}^2$).

(2) **Process of crystallization of the glass during heat treatment.** Thermal differential and X-ray analysis made with the glass specimen of above composition